PRF # 58518-ND9
Project Title: STABILITY OF SURFACTANT SYSTEMS FOR OIL MOBILIZATION
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The goal of this proposal is to investigate the stability of surfactant solutions and the rheology of surfactant colloidal systems at the oil-water interface. During the reporting period:

(a) We determined first the appropriate computational protocol for investigating oil-gas interfaces with surfactants and particles.
(b) We investigated the stability of interfaces when hydrophobic particles (i.e., carbon nanotubes) and surfactants are present.
(c) We also started to investigate models with amphiphilic (Janus) particles as vehicles to transport surfactants to the oil-brine interface.
(d) Finally, we worked on developing computational experiments that will allow us to study the behavior of single surfactant molecules or single Janus particles with adsorbed surfactants under controlled shear and elongational stress fields.

More details are offered below:

(a) Computational experiment protocols [1]. We developed a systematic approach for using Dissipative Particle Dynamics (DPD) techniques to simulated anionic surfactants (such as sodium dodecyl sulfate) and nonionic surfactants (such as octaethylene glycol monododecyl ether) in oil-water interfaces. The key was to place the theoretically calculated number of surfactant molecules on the interface at the critical micelle concentration. Based on this approach, the molecular description of surfactants and the effects of various interactions parameters on the interfacial tension were calculated. We found that the interfacial tension is affected mostly by the head-water and tail-oil interactions parameters. Even though the procedure was used with DPD, we believe that it can be applied for other coarse-grained methods to describe the surfactant behavior on the oil-water interface. This work was the necessary step in ensuring that the computations would be relevant to physical situations and would be trusted to model accurately oil-water interfaces with surfactants and particles.

(b) Interfaces with carbon nanotubes (CNTs) used to deliver surfactants to the oil-water interface [2]. Two different surfactants were considered, the anionic sodium dodecyl sulfate (SDS) and the nonionic octaethylene glycol monododecyl ether (C12E8). It was found that the electrostatic effect of the anionic surfactant and the steric effect of the nonionic surfactant negatively affected the adsorption process. On the oil-water interface, the surfactant molecules quickly desorbed from the CNT to distribute on the interface, leading to significant reduction of the oil-water interfacial tension. At low surfactant concentration, the CNTs also remained on the interface, reducing further the interfacial tension. These results suggest that carbon nanotubes, or other hydrophobic nanoparticles, can be good candidates for delivering surfactants for applications like enhanced oil recovery.

(c) Janus particles and surfactants at the oil-water interface [3]. Systems that included spherical nanoparticles with different patterns of wettability on a water-heptadecane interface with the presence of sodium dodecyl sulfate were examined. The coverage of the interface by nanoparticles and the concentration of surfactants were systematically changed. Results showed that the synergies of nanoparticles and surfactants reduce the oil-water interfacial tension further than surfactants alone. It was found that the effective surfactant concentration on the oil-water interface, which was left available to surfactants when the nanoparticles were also present, is the key factor affecting the interfacial tension. These results lead to the development of guiding principles for the design (or selection) of appropriate surfactant molecules to stabilize particle-surfactant emulsions.

(d) Development of computer experiments with controlled hydrodynamic stress fields. We developed DPD-based models with simulations of a four-roll mill setup in order to conduct rheological computer experiments. Our focus was to develop a shear field that would be completely elongational. By turning the four mill cylinders at a specified rotation rate, we validated the velocity and stress field with water only. This year we will add long surfactant molecules in the center of the four-roll mill setup and subsequent runs will involve the Janus particle with the adsorbed surfactants. We plan to use these simulations to characterize the surfactant adsorption and to determine the critical extensional stresses for surfactant dissociation from the particle surface.

References (publications with partial PRF support)

1. Vu, T.V., and D.V. Papavassiliou "Oil-water interfaces with surfactants: a systematic approach to determine coarse-grained model parameters," *J. Chem. Phys.,* **148**, Art. 204704 (11 pages) 2018; DOI: 10.1063/1.5022798
2. Vu, T.V., and D.V. Papavassiliou, "Modification of oil-water interfaces by surfactant-stabilized carbon nanotubes," *J. Phys. Chem. C*, **a122**, 27734-27744, 2018; DOI: 10.1021/acs.jpcc.8b08735
3. Vu, T.V., and D.V. Papavassiliou, "Synergistic effects of surfactants and heterogeneous nanoparticles at oil-water interface: Insights from computations," *J. Colloid & Interf. Sci.,* **553**, 50-58, 2019; DOI: 10.1016/j.jcis.2019.05.102